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On the Possibility of Electrochemical Processing of Dump Industrial Iron-Antimony Matte

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Abstract

One of the most important and urgent problems facing the metallurgical industry is the problem of processing dump mattes (DM). These are alloys of sulfides of various metals, and in some locations have accumulated to such an extent that they fill entire landfills with environmentally hazardous substances. During prolonged storage in air, DM decomposes and produces toxic substances. Therefore it is important to find an environmentally safe way to store or processes DM. The available information on the technologies for processing sulfide-oxide metallurgical raw materials and sources of DM formation are analysed in this study. Chemical analysis of the DM indicates a high iron content, which *a priori* determines the high conductivity of dump materials. The aim of this research is to examibne the physicochemical properties of the DM melts of the Kadamjai antimony industrial complex, in which, according to the technological schedule, iron and antimony are accumulated in sulfide form, followed by pyroelectrochemical processing of them into commodity products in the case of optimal metal current yields and good extraction. The electrical conductivity (æ) of the industrial DM melt is characteristic of multifunctional conductors with a predominant semiconductor mechanism of conductivity. The addition of a heteropolar additive (Na_2S) into the DM melt suppresses the electronic component of conductivity and decreaseds æ in the system to values that are typical for ionic melts. Current-voltage characteristics for the composition of the system with 60 and 70 mol. % Na_2S indicate polarization in the melts. The electrolysis of DM-Na_2S melts is accompanied by the release of sulfur on the anode. For a final assessment of the possibility of using electrochemical processing of DM melts into antimony metal, it is recommended that a preliminary economic calculation of the entire technological process be performed.

Keywords: dump mattes, iron and antimony sulfides, physicochemical properties, ecology, utilization

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The study of the electrochemical and electrophysical properties of sulfide melts attracts scientists and metallurgists in the first place because sulfide and sulfide-oxide poly-metallic ores are the raw materials for the industrial production of metals such as antimony, bismuth, copper, nickel, cobalt, lead, tin, zinc.

In addition, one of the most important and urgent problems of the metallurgical industry is the problem of processing dump mattes (DM), which are alloys of sulfides of various metals. They form entire polygons of environmentally hazardous substances when accumulating. During long-term storage of DM in air, its phase composition changes. The most likely processes contributing to this are hydration, carbonization and hydrolysis of the components of the DM under the influence of atmospheric moisture and carbon dioxide.

In many technological schemes raw materials are specially melted into matte, into which the bulk of the metal is extracted. In others, the processing of sulfide ores and concentrates by pyrometallurgical methods is accompanied by the formation of mattes as ballast products which part of the smelted metal passes into. The metal-rich part of the matte is returned to the process and, thus, it circulates in a closed circle. The metal-depleted part of the matte is sent to the dump.

As a result, the fraction of recoverable metal is significantly reduced and, accordingly, its price is rising. Hence, it seems relevant to study the physicochemical properties of the DM in order to select the most effective method for their disposal. The iron-antimony DM of the pyrometallurgical method for producing antimony contains (wt. %): up to 7 % Sb, 55 % Fe, and 30 % S. The amount of formed matte is quite large and comes to 20-25 % of the mass of the concentrate to be processed.

The aim of the research is to study the physicochemical properties of the DM melts of the Kadamjai antimony industrial complex, in which, according to the technological schedule, iron and antimony are accumulated in sulfide form, followed by pyroelectrochemical processing of them into commodity products in the case of optimal metal current yields and good extraction.

Based on the theoretical concepts of A. A. Velikanov et al. [1] on the multifunctionality of conductivity, molten sulfide systems require a special approach when considering issues related to their electrochemical conversion to metal.

In particular, according to theoretical concepts, such ion-electron melts (multifunctional conductors - MFC) can be brought to a state in which they can be electrolyzed with high rates, by increasing the polarity of the bonds by introducing typically ionic substances (heteropolar additives - HA).

Given that MFC has a significantly narrower band gap than the ionic conductor additive, it can be assumed that the essence of the effect of the additive is to increase the band gap of the MFC. The correlation between the ion contribution and the amount of HA was considered in [2] as an example of a specific Sb_2S_3 – Na_2S system in which the conductivity (æ) naturally decreases with an increase of Na_2S (HA). It associates with the partial transformation of chemical bonds in non-ferrous metal sulfide under the

influence of HA, accompanied by an increase of ionic nature carriers. In some cases, when the electrolytic decomposition of an individual substance is practically impossible, the introduction of HA can change the ratio of contributions in favor of ionic one, and electrolysis of systems becomes effective [2].

According to our research, dump iron-antimony mattes (DM) of precipitating-reducing smelting of antimony concentrates have a specific gravity in the range of 4-5 g/cm^3. The chemical composition of mattes for the main components is illustrated in Table 1. The main mass. % is iron, antimony is in the form of $NaSbO_2$ and $NaSbS_2$ in matte.

Table 1: The average composition of pyrometallurgical dump matte (DM).

Elements that were defined	$Sb_{general}$	Fe	$S_{general}$
Content, mass. %	5,72	36,69	23,33

The presence of iron sulfide with high conductivity in the DM obviously makes it impossible to electrochemically process their melts. Therefore, previously, to determine the nature of the conductivity of the melt of an individual DM, its electrical conductivity (æ) was studied. An industrial matte of precipitating-reducing smelting of the Tereksai flotation concentrate of the metallurgical shop of the Kadamjai industrial complex was used as the initial DM. To determine the æ values of the melts, the four-electrode direct current method was used.

The values of the electrical conductivity of an individual DM are shown in Figure 1.

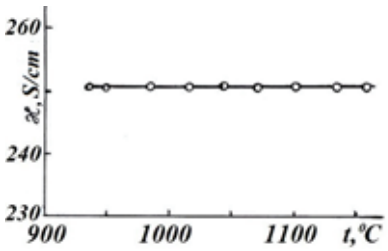

Figure 1: The temperature dependence of the conductivity of an individual DM.

In the temperature range of 986-1158 ˚C, the value of æ DM varies from 250.83 to 248.70 S/cm and has a negligible negative temperature coefficient, which indicates a significant non-ionic contribution to the conductivity of DM, which is due to the presence of highly conductive iron sulfide (see Table 1).

To transform the nature of the conductivity of DM, sodium sulfide was used as a hydrodynamic compound. Six samples were prepared (Table 2) of the DM-Na_2S system at a rate of 30-80 mol. % Na_2S relative to FeS contained in the DM.

Before fusion, DM were dried in a vacuum oven over calcium chloride. Sodium sulfide was prepared by dehydration of a reactive preparation, qualification of «analytical reagent grade», heating in vacuum, followed by long-term drying in a vacuum oven over

Table 2: The composition of the samples of the DM - sodium sulfide system.

№ of sample	Mass % Na_2S	Mol. % relative to FeS
1	15,90	30
2	21,45	40
3	27,16	50
4	32,96	60
5	38,95	70
6	45,07	80

phosphorus oxide (V) at 200 °C. The calculated quantities of the starting materials were thoroughly mixed in a dry box, transferred to glassy carbon crucibles, placed in quartz reactors, which were evacuated, filled with an inert gas, and heated until the reagents melted. In the molten state the samples were kept for one hour, then cooled.

The electrical conductivity of the obtained samples was measured in the temperature range 700–900 °C (Figure 2).

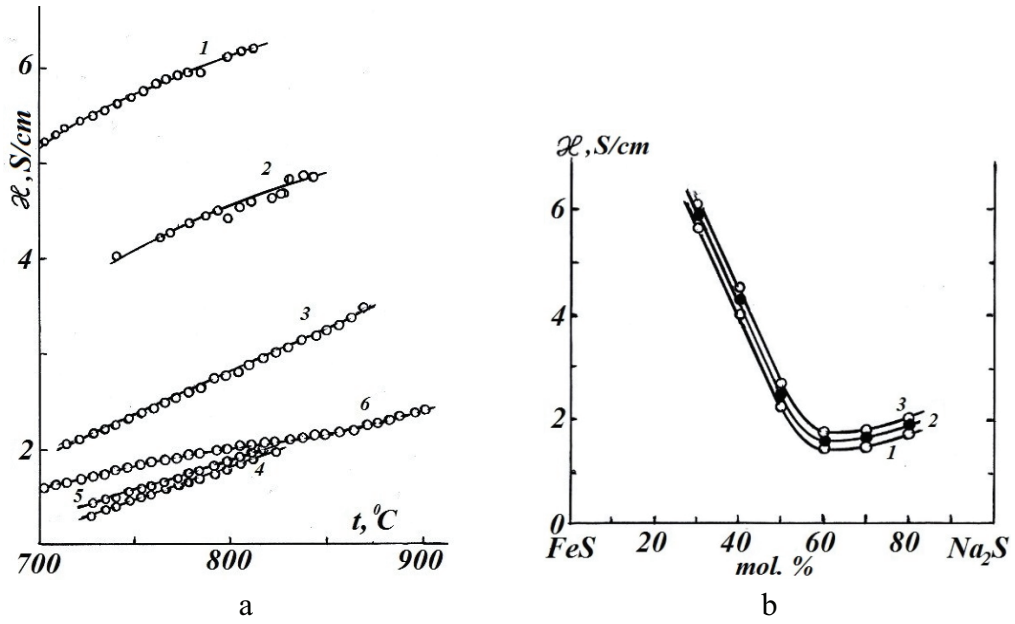

Figure 2: Polytherms (a) and isotherms (b) of the electrical conductivity of the melts of the DM - Na_2S system at 30 (1); 40 (2); 50 (3); 60 (4); 70 (5); 80 (6) mol. % Na_2S, for 740 (1); 766 (2); 792 (3) °C.

The temperature dependence of the electrical conductivity of the molten DM and its high values suggest that the studied system is a MF with a predominance of carriers of electronic nature. According to [1, 2], the main role in semiconductor conductivity is played by semiconductor and metal contributions, that is, to a large extent we are dealing with a degenerate semiconductor. Hence, it follows that in an individual form, the DM melt cannot be decomposed by electrolysis with positive results.

An analysis of the temperature dependences of the electrical conductivity of the DM-Na_2S system shows that it is possible to reduce the high values of æ of the individual DM by introducing HA. In this case, the form of the æ - t dependence becomes characteristic of conductors with a predominant ionic contribution to conductivity. An increase of HA in the melt is accompanied by a decrease in æ, which passes through a minimum for a composition with 60 mol. % Na_2S, after which æ increases slightly. Obviously, with this ratio of components, the maximum suppression of the electronic component was achieved, and this region of compositions is most favorable for electrolysis.

The polarization characteristics of the samples were determined by the Leblanc process in alundum tubes in an inert atmosphere. The area of graphite electrodes was 0.125 cm^2. The results of the study are presented in Table 3 and Figure 3.

TABLE 3: The polarization characteristics of the melts of the DM - Na_2S system, depending on composition and temperature at interelectrode distance of 2 cm.

Temperature, ˚C	Decomposition Voltage		
	E_1, B	E_2, B	E_3, B
Polarization characteristics for the DM –Na_2S melt (sample № 4)			
901	-	-	1,68
869	0,56	1,74	-
837	0,67	1,76	-
805	0,40	0,80	1,98
Polarization characteristics for the DM –Na_2S melt (sample № 5)			
901	-	-	1,95
869	0,22	1,86	-
837	0,30	1,86	-
805	0,36	1,06	1,92
773	0,42	1,08	2,24

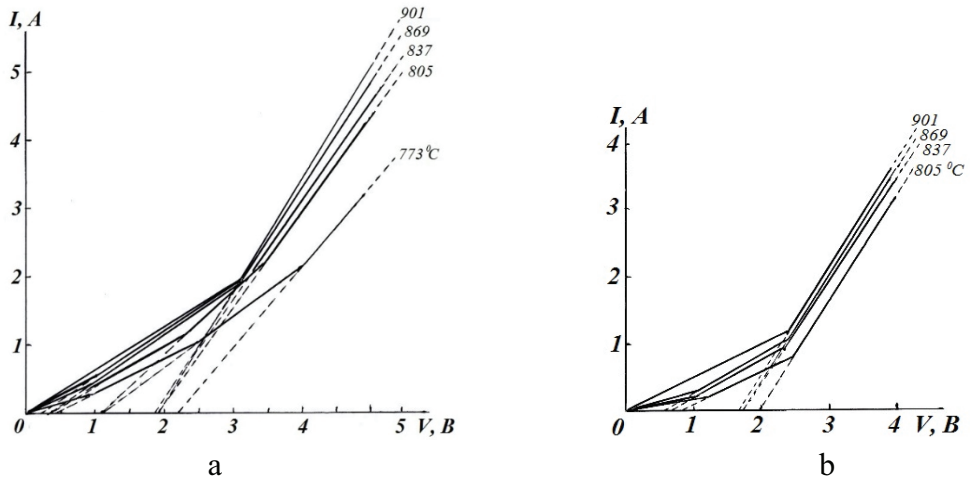

Figure 3: Polarization characteristics of DM melts with 60 mol. % Na_2S (a) and 70 mol. % Na_2S (b) relative to FeS.

On I-V dependencies for compositions with 60 and 70 mol. % Na_2S fixed clear kinks. This suggests that the ionic mechanism of charge transfer plays a significant role in the conductivity of these melts. At higher temperatures a single kink appears in the polarization curves, which should be related to the decomposition of Na_2S. At lower temperatures the curves show two kinks, the first of which is associated with the release of antimony metal. And finally, at the lowest temperatures on the IV dependences, three kinks appear already; the second of them is most likely due to the decomposition of FeS.

For the electrolysis of melts of the DM - Na_2S system, in accordance with the obtained data on electrical conductivity and polarization, compositions containing 60 and 70 mol. % Na_2S with respect to FeS, which are in the field of electrochemical efficiency [2]. Electrolysis was carried out at temperatures of 770-840 °C. In various experiments, voltages from 1.5 to 6 volts were applied to the terminals of the electrolysis bath. The cathode current density was varied in the range of 0.3-7 A/cm^2. The duration of electrolysis is 4-8 hours. In all experiments stratification of the melts was observed. Chemical analysis showed that the near-cathode layer is enriched in antimony sulfide, and the anode layer is enriched in sodium sulfide. Sulfur vapor condenses on the walls of the reactor. None of the experiments show significant amounts of metal.

It should be noted that the absence of metallic antimony in the cathode space does not yet indicate a partial suppression of the electronic contribution. The presence of electrochemical changes in the system is evidenced by the release of sulfur, which settles on the walls of the electrolyzer, as well as a constant change in the current strength in the circuit. Obviously, in this multicomponent system, depolarization phenomena prevail over polarization phenomena. The resulting metal is capable of dissolving in the melt and interacting with liquid products, which is accompanied by strong convection currents.

Findings. The conductivity of the industrial DM melt is characteristic for MFC with a predominant semiconductor conduction mechanism. The introduction of HA into the DM melt is accompanied by the suppression of the electronic component of conductivity and a decrease in æ in the system to values characteristic of ionic melts. Current-voltage characteristics for the composition of the system with 60 and 70 mol. % Na_2S indicate polarization in the melts. The electrolysis of DM - Na_2S melts is accompanied by the release of sulfur on the anode. For a final assessment of the possibility of using electrochemical processing of DM melts into antimony metal, it is recommended that a preliminary economic calculation of the entire technological process be performed.

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